AN INVESTIGATION OF SOME REACTIONS OF THE PHOTODIMER OF 9-CHLOROANTHRACENE.

BY

MARY-DELL MATCHETT

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THESIS
FOR THE
DEGREE OF BACHELOR OF SCIENCE
IN
CHEMISTRY

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COLLEGE OF LIBERAL ARTS AND SCIENCES
UNIVERSITY OF ILLINOIS
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The author wishes to thank Dr. D.E. Applequist for the time and effort which he spent in directing this research.
Abstract

This thesis describes an investigation of the reactions of n-butyllithium, phenyllithium, and p-tolylithium with 9,10'-dichlorodianthracene. Dianthracene was found to be a product of all three reactions, and 9-chlorodianthracene was found to be a product of the latter two. Since analogous treatment of 9,10'-dibromodianthracene with methyl- and n-butyllithium has been shown (1) to produce 9-methyldianthracene and 9-n-butyldianthracene, respectively, an attempt was made to synthesize 9-phenyldianthracene for comparison with unknown products from the phenyllithium reaction. Although the monomer 9-phenylanthracene was synthesised, it was found not to form a mixed photodimer with anthracene. Several attempts to synthesise the monomer 9-p-tolylanthracene were unsuccessful. No substance was found among the products of the phenyllithium reaction whose melt had an infrared spectrum similar to that of a 1:1 molar mixture of anthracene with 9-phenylanthracene. Thus no evidence of the presence of 9-phenyldianthracene was found.

From all three reactions of 9,10'-dichlorodianthracene studied, different high-melting thermostable hydrocarbons were isolated. The n-butyllithium hydrocarbon had a different melting point from that found by an earlier worker (3). Its melting point and carbon hydrogen analysis indicated, and its ultraviolet spectrum confirmed its identity to be 9,10'-dehydrodianthracene, a known compound (1).

The phenyllithium and p-tolylithium hydrocarbons, as well as a known sample of 9,10'-dehydrodianthracene were studied by nuclear magnetic resonance at elevated temperature, using molten naphthalene as a solvent and ferrocene as a quantitative and qualitative standard. Comparison of peak areas indicated the empirical formulae of the unknown hydrocarbons to be $C_{34}H_{22}$ and $C_{35}H_{24}$, for the phenyl- and p-tolylithium products, respectively. The most likely structures for these compounds are 9-aryl-9',10-dehydrodianthracenes, although 9-aryl-9', 10'-dehydrodianthracenes have not been ruled out as possibilities.
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I. Introduction

The photodimers of 9-chloro- and 9-bromoanthracene have been found to produce upon treatment with various lithium reagents varying amounts of dianthracene, other unidentified lower melting ($180^\circ$) products, 9-alkylated dianthracenes (from 9,10'-dibromodianthracene upon treatment with alkyl lithium reagents), and varying yields of high-melting hydrocarbons in which new carbon-carbon bonds appear to have been formed. In the case of 9,10'-dibromodianthracene, treatment with phenyllithium has been shown by D.E. Applegquist (1) to produce the hydrocarbon 9,10'-dehydrodianthracene in 80% yield. Treatment with n-butyllithium or methyllithium produces the same hydrocarbon, but in low yield, the former producing chiefly 9-n-butylidianthracene, the latter, dianthracene. In the case of 9,10'-dichlorodianthracene, E.C. Friedrich (3) found that treatment with either phenyllithium or n-butyllithium produced in low yield a hydrocarbon melting at 323-324$^\circ$. The analysis of this compound indicated its composition to be $C_{20}H_{18}$. However, treatment with p-tolylolithium produced a different hydrocarbon (m.p. 356-357$^\circ$) whose analysis indicated its composition to be $C_{20}H_{20}$. The structure 9,10'-dehydrodianthracene was proposed for the $C_{20}H_{18}$ hydrocarbon, but no reasonable structure could be imagined for the $C_{20}H_{20}$ hydrocarbon consistent with IR and UV spectral indications of great similarity to the structure of the $C_{20}H_{18}$ hydrocarbon.

Attempts by E.C. Friedrich to incorporate deuterium into these hydrocarbons by destroying the lithium reagent prior to reaction workup with $D_2O$ resulted in no significant amount of incorporation. This result was not surprising, for tertiary lithium reagents have been shown to be capable of abstracting protons from organic solvents.

R. Little (4) attempted to incorporate deuterium into the $C_{20}H_{18}$ hydrocarbon from the phenyllithium reaction by use of the starting material 9,10'-dichlorodianthracene-9',10'-D, which he synthesized. The hydrocarbon was isolated, but
exhaustive purification failed to bring its melting point above 305-310°. A deuterium analysis was therefore not made.

The aim of this research was to study the reaction of 9,10'-dichlorodi-anthracene with phenyl-, p-tolyl-, and n-butyllithium in hopes of elucidating the structures of the high-melting hydrocarbons formed and of isolating and identifying the other lower melting products of these reactions.
II. Discussion

There are a number of reactions which might be anticipated to occur between lithium reagents and the photodimers of 9-haloanthracenes. In the following reactions, the benzene rings in the dimeric structure are omitted for the sake of simplicity.
Reactions of this general type were first studied in hopes of finding an X and an R such that reaction 4 would occur, or perhaps even reaction 5. The double bonds in VIII and IX would be interesting to study, since they occur at two bridgehead carbon atoms. At present no evidence has been found that either of these reactions occurs, although it is possible that a bridgehead double bond occurs in an intermediate in the reactions of aryl lithium reagents with 9,10'-dichlorodianthracene, as will be shown.

Reaction 1 has been found to occur to a greater or lesser extent in all reactions of this type thus far studied. Its product, dianthracene (I) has long been known.

Reaction 2 has been found to occur in 80% yield upon treatment of 9,10'-dibromodianthracene with phenyllithium. The structure of II was elucidated by means of a deuteration experiment reported by D.R. Applequist (1). When 9,10'-dibromodianthracene-9',10-D was treated with phenyllithium, II was isolated and
found to contain two deuterium atoms per molecule. Since the structure of 9,10-dichlorodibenzanthracene was shown to be head-to-tail by measurement of its dipole moment (1), the possible isomers VIII and X were ruled out.

In order to study further the properties of the high melting hydrocarbons as yet unidentified, the reactions run by previous workers were repeated. Samples of 9,10'-dichlorodibenzanthracene were treated with phenyllithium and p-tolylolithium and the respective hydrocarbons isolated and found to have the melting points previously reported (5). However, treatment with high purity n-butylithium manufactured by Foote Mineral Co. (distilled during manufacture to remove contaminants and thereafter stored under an inert atmosphere) failed to produce any detectable amount of the previously reported hydrocarbon (m.p. 322-323°) but instead produced in low yield 9,10'-dehydrodibenzanthracene, II (m.p. 370°) whose identity was confirmed by comparison of its ultraviolet spectrum with that of the known compound and by analysis.

Extensive fractional crystallisation of the products of the p-tolylithium reaction yielded successive crops of white crystals with generally decreasing melting points and depressed recrystallisation points, all of whose infrared spectra were very similar. A careful recrystallisation of a portion of this material, discarding the first crop which appeared to contain a small amount of the high melting hydrocarbon, yielded white crystals whose melting and recrystallising and mixed melting points with an authentic sample of a 1:1 molar mixture of anthracene and 9-chloroanthracene indicated it to be 9-chlorodibenzanthracene, III, where X is Cl. The presence of halogen was confirmed by a strong positive Biehlstein test. An infrared spectrum of the melt of this material was identical to that of an unauthentic 1:1 molar mixture of anthracene and 9-chloroanthracene.

A substance (m.p. 215°, remelt 160°) isolated by R. Litle (4) from his reaction of phenyllithium with 9,10'-dichlorodibenzanthracene in 22% (by weight) yield was also studied. In an attempt to identify this material as 9-phenyldi-
anthracene, 9-phenylanthracene was prepared by treatment of anthrone with phenylmagnesium bromide. A low yield was obtained. (Repeated attempts to prepare 9-p-tolylanthracene by the analogous treatment of anthrone with p-tolylmagnesium bromide failed.) An attempt to form the mixed dimer of anthracene and 9-phenylanthracene produced only dianthracene and unreacted 9-phenylanthracene. Although the mixed melting point of a melted 1:1 molar mixture of anthracene and 9-phenylanthracene with the unknown after melting was not depressed significantly, infrared spectra of the known and unknown mixtures indicated that the two were not identical. Analysis of the unknown indicated the presence of one chlorine atom. Investigation of mixed melting points and comparison of infrared spectra of an authentic 1:1 molar mixture of 9-chloroanthracene with anthracene and the melt of the unknown indicated the two to be identical. The unknown was thus identified as a 9-chlorodolanthracene, III, where X is Cl. Independently synthesized 9-chlorodolanthracene prepared by E.L. Friedrich (3) melted 203-205°, remelted 150-163°.

Since 9-p-tolylanthracene had been reported to be successfully prepared from treatment of o-benzylbenzoic acid with p-tollyllithium (2), and since 9-p-tolyldianthracene was suspected to be a principle product of the p-tollyllithium reaction with 9,10'-dichlorodulanthracene, o-benzylbenzoic acid was reduced to o-benzylbenzoic acid according to the modified Clemmensen reduction suggested by E.L. Martin (5). The yield was 62.5%. Since the principle product of the dimer’s reaction with p-tollyllithium appeared to be 9-chlorodolanthracene, the synthesis of 9-p-tolylanthracene was not completed.

The nuclear magnetic resonance spectra of I, II, and the unknown high-melting hydrocarbons resulting from treatment of 9,10'-dichlorodolanthracene had never previously been observed because of the extremely low solubility of these compounds in customary NMR solvents at room temperature. The solvents CC1₄, CHCl₃, C₂H₂Cl₂, CS₂, liquid SO₂ and C₆H₆ all were tested both at room temperature
and at elevated temperature, but none proved satisfactory. However, when fused naphthalene was used, an 8-10% solution of II and of the two unknown hydrocarbons could be obtained at 110-150°. (Compound I was much less soluble, even in this solvent.) Sample tubes were prepared for each using ferrocene (τ=5.95) as a qualitative and quantitative standard. The tubes were sealed carefully under high purity nitrogen to prevent oxidation of the ferrocene. Nuclear magnetic resonance spectra of these samples were obtained at temperatures of 110-150°. Assuming the ferrocene peak to be unaltered in chemical shift under these unusual solution conditions, the hydrocarbon spectra showed the following peaks: 9,10'-dehydrodianthracene, a single peak at τ=4.96; phenyllithium's product, a single peak at τ=5.00; p-tolyllithium's product, one peak at τ=4.99 and another at τ=7.62 (in the region of aryl -CH₃). Peak areas were compared with the ferrocene peak's area (concentrations having been made such that the latter represented two hydrogens, so that the peaks would be of comparable size). Results indicated that 9,10'-dehydrodianthracene had two bridgehead hydrogens, the unknown from the phenyllithium reaction, one, and the unknown from the p-tolyl-lithium reaction, one half, with three halves of a hydrogen in the region of aryl methyl. This last sample was evidently not completely in solution, but since the aryl -CH₃ can be used as an internal standard, a single bridgehead hydrogen is indicated. (The presence of two p-tolyl substituents and two bridgehead hydrogens is excluded by the fact that such a structure would be dimeric and would not melt reversibly, as the unknown does.) These data suggest two structural possibilities for the unknown hydrocarbons: V or VI, where R is phenyl or p-tolyl. The analyses of the pure hydrocarbons reported by R.C. Friedrich (3) are consistent with these structural formulas. For the phenyllithium product:

**Anal.:** Calcd. for C₃₈H₂₂: C, 94.85; H, 5.15.

**Found: C, 95.03; H, 5.30**

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For the p-tolyllithium product:

**Anal.** Calculated for C₃₅H₂₄: C, 94.5%; H, 5.5%.

Found: C, 94.5%; H, 5.4%.

Supporting evidence for either of the above possibilities was furnished by an experiment in collaboration with F. Litter, who synthesized 9,10'-dichloro-dianthracene-9',10-D, treated it with phenyllithium, and isolated the unknown hydrocarbon but did not succeed in purifying it adequately (m.p. 305-310°C).

This compound has now been further purified by fractional sublimation and, although still not pure (m.p. 312-317°C), it was submitted for deuterium analysis. This analysis indicated clearly that one deuterium per molecule was present, although the atom per cent found was half a per cent (absolute) higher than that calculated for the structures suggested above. This error can be attributed to the presence of contaminating 9,10'-dehydrodianthracene-9',10-D, which one might expect to be formed to a greater extent in this reaction than is II from the non-deuterated dimer. Because of a slower rate of metatation at the C-D site than at C-H, exchange at C-Cl can occur to a greater extent in the deuterated dimer, as shown in reaction 2.

One can account for the formation of V by either reaction 3-a or reaction 6-a. Of these, 6-a seems less likely because of its competition with 5-b.

Analogously, an attempt to produce 9-phenylanthracene from 9-chloroanthracene with phenyllithium under conditions identical to those of the above reactions produced no detectable amount of the former, but only anthracene.

One can account for the formation of VI by reaction 3-b-l. Since this reaction is in competition with 3-a, whose product is V, and since only one thermally stable product, not a mixture, appears to result, addition of the lithium reagent to IV must occur preferentially one way. A concerted addition may occur, without the intermediates shown. In either case, the existence of IV, which has a bridgehead double bond, seems likely.
The fact that chemical shifts for the bridgehead hydrogens in II and in the two unknown hydrocarbons are so nearly identical may indicate VI as a more likely structure for the hydrocarbons than VII. Unfortunately, 9,9'-dehydrodi-anthracene, X, is not a known compound; the chemical shift of its bridgehead hydrogens is therefore not available for comparison.
Experimental

All melting points are uncorrected. The author is grateful to J. Nemeth for microanalyses, O. Norton for nuclear magnetic resonance spectra, R. Johnson for infrared spectra, and C. Juan for ultraviolet spectra.

Reaction of Phenyllithium with 9,10-Dichlorodanthracene.- Phenyllithium was prepared by the method of Organic Reactions (7) on one tenth the scale to give a 1.104 molar solution of phenyllithium in anhydrous ether. To a solution of 2.0 g. (0.046 mole) of 9,10-dichlorodanthracene(a) in 200 ml. of warm anhydrous benzene under a nitrogen atmosphere was added 25 ml. of the above phenyllithium solution. After 17 hours at reflux, the solution was treated cautiously with 100 ml. of distilled water and refluxing was continued for an hour. The resulting mixture was filtered while warm to remove a small amount of grey interfacial solid, the organic layer separated and benzene solvent removed by distillation. The residue was overheated, hence any dimeric substances which were present were monomerized. The brown oil which remained was dissolved in cyclohexene, treated with Darco, filtered, and diluted with ether. A fine precipitate of white prisms was filtered off and observed to be 0.21 g. of a substance melting reversibly at 303-310°. The infrared spectrum of this substance indicated that it was the same as that isolated by E.C. Friedrich (3). A recrystallization from cyclohexene brought the melting point up to 312-314°. (These melting points were taken in an air bath instrument which was later shown to give low readings at high temperatures.)

When this reaction was run under similar conditions and benzene solvent removed from the products by evaporation on a steam bath, from 2.0 g. of dimeric starting material, 2.43 g. of solid products were isolated, of which 0.25 g. was separated by fractional crystallization from cyclohexene and found to be dianthracene, in 15.5% yield.

(a) Provided by D.E. Applequist.
When this reaction was run by R. Little on 10 g. of dimeric starting material, an unknown substance was isolated from the cyclohexene solution of reaction products (after removal of three crops of higher melting substances) by trituration of the solution, now concentrated to 30 ml., with petroleum ether. This substance, m.p. 195-215°, weighed 2.2 g. Upon recrystallization from acetone, three successive fractions were isolated by him, but no further analysis was pursued. All three have now been found to melt irreversibly at 216°, the first remelting at 160°. Comparison of the infrared spectrum of the melt of this material with those of a 1:1 molar mixture of 9-phenylanthracene with anthracene and of a 1:1 molar mixture of 9-chloroanthracene with anthracene revealed that the unknown mixture was identical to the latter. E.C. Friedrich reported (3) that 9-chlorodianthracene, which he synthesized by photodimerization, melted at 203-205°, remelted from 150-163°.

**Anal.:** Calcd. for C₂₈H₁₉Cl: C, 86.07; H, 4.36

**Found:** C, 84.55; H, 4.61.

When this reaction was run by R. Little on 8.9 g. of 9,10'-dichlorodianthracene-9',10'-D prepared by him, 3.2 g. of the crude high melting hydrocarbon was isolated in the following way: The benzene solution of reaction products, after destruction of excess lithium reagent with water, was separated and allowed to cool. Crude dianthracene was then filtered off (1.7 g., m.p. 250-260° with sublimation) and benzene solvent evaporated from the filtrate. The remaining solid was digested with cyclohexene and 3.2 g. of solid filtered off, m.p. 200-280°. After three pyrolyses and recrystallizations from cyclohexene, Little isolated 0.116 g. of white prisms melting at 305-310°. No further purification was attempted by him because the sample was small. This material has been sublimed fractionally in an attempt to effect further purification. A 95 mg. sample of the hydrocarbon was sublimed at 100-110°, 0.6-1.0 mm. Hg, for 48 hours. The small amount of sublimate collected melted at 290°. The oil bath temperature
was then raised to $240^\circ$ and sublimation continued at $245-267^\circ$, 0.3 mm. Hg. Two fractions were taken from the condenser surface; the outermost 30 mg. melted at $310-317^\circ$; the innermost 50 mg. melted $308-310^\circ$. A sample of the outer fraction was submitted for deuterium analysis. The inner fraction was used for carbon-hydrogen analysis.

Anal.: Calcd. for $C_{34}H_{21}D$: C, 94.6; H, 5.3; D, 4.55 abs. atom %.
Found: C, 94.12; H, 5.22; D, 5.01 abs. atom %.

9-Phenylanthracene.—This procedure was adapted from one of Schlenk and Bergmann (8). To 12.2 g. (0.50 g. atom) of magnesium in 75 ml. of anhydrous ether under a nitrogen atmosphere was added dropwise a solution of 35 g. (0.22 mole) of bromobenzene in 50 ml. of anhydrous ether while the mixture was stirred. To the resulting solution of phenylmagnesium bromide was added 19.4 g. (0.10 mole) of anthracene. The solution formed (green by transmission, blue by reflection) was heated under reflux for three hours and allowed to stand overnight. The excess Grignard reagent was destroyed with cracked ice and dilute hydrochloric acid. To this mixture was added hydrosulfite and sodium hydroxide, and the mixture heated at reflux for two hours. This mixture was cooled, and the yellow crude hydrocarbon skimmed from the surface. After several recrystallizations from acetone, 1.56 g. of 9-phenylanthracene (6.25% yield) was obtained, m.p. $145-146^\circ$. Reported m.p.: $152^\circ$ (8).

Attempted Photodimerization of Anthracene with 9-Phenylanthracene.—A solution of 0.0509 g. (0.0002 mole) of 9-phenylanthracene and 0.0356 g. (0.0002 mole) of anthracene in anhydrous benzene was sealed in a pyrex test tube and irradiated under a 275 watt sun lamp for three days. (Because of failure to sweep the tube with nitrogen, a small amount of oxidation occurred, the solution becoming amber after eight hours.) The reaction mixture was filtered and the white crystals rinsed with benzene and 15 ml. of boiling acetone. The remaining solid (m.p. $268-270^\circ$, remelt $200^\circ$) was assumed to be dianthracene. The brown
benzene solution was evaporated to dryness and the resulting solid recrystallized from acetone with Darco, a few drops of water being added. The resulting yellow-orange grainy crystals (m.p. 146°) did not depress the melting point of pure 9-phenylanthracene.

2-Chloroanthracene. — According to the method of Mikhailov and Promyslov (6), 26 g. (0.147 mole) of anthracene, 36.5 g. (0.175 mole) of phosphorus pentachloride, and 350 ml. of dry benzene were heated on a water bath in a flask fitted with a reflux condenser and calcium chloride drying tube. The mixture was heated at 80° for 50 minutes after it became red. At the end of this time, all material had dissolved. The dark red solution was allowed to cool overnight. The benzene solution was washed cautiously with 350 ml. of water, and again with 250 ml. The benzene solution was dried briefly over sodium sulfate and the solvent was evaporated. The dark green residue was extracted with boiling ethanol in two successive 350 ml. batches. The first crop from each was contaminated with a higher melting material (probably 9,10-dichloroanthracene), but the second crop from each was pure 9-chloroanthracene in long flat needles (m.p. 101-102°). Literature m.p.: 106° (6). The pure product weighed 1.80 g. (5.74% yield).

Reaction of 9-Chloroanthracene with Phenyllithium. — To a solution of 1.80 g. (0.0095 mole) of 9-chloroanthracene in 100 ml. of warm anhydrous benzene was added 23 ml. of 1.512 N phenyllithium prepared according to the method of Organic Reactions (7). This mixture was heated at reflux under a nitrogen atmosphere for 17 hours, at the end of which time the excess lithium reagent was destroyed with water, the mixture filtered and the benzene layer separated, dried, and evaporated to dryness. The residue was extracted with ether and the undissolved portion, yellow-white grainy crystals, melted sharply at 216°. They had an infrared spectrum identical with that of anthracene. No crystalline products were obtained from the ether extract.
**o-Benzylbenzoic Acid.** According to the method suggested by E.L. Martin (5), an aqueous solution of 0.1 g. of copper sulfate pentahydrate crystals was allowed to stand in contact with 25 g. (0.382 g. atom) of zinc dust for a few minutes. The solution was then poured off and to the activated metal were added 400 ml. of 2.0 N sodium hydroxide, 100 ml. of toluene, and 15 g. (0.0675 mole) of o-benzyolbenzoic acid. This mixture was heated at reflux for 13 hours and allowed to stand for three days. The two phase system was separated and the organic portion evaporated to dryness, leaving only a small amount of oily residue. The aqueous layer was neutralized by cautious dropwise addition of concentrated sulfuric acid. A white precipitate came down continuously. When the solution was acid to litmus, it was cooled and the product collected and rinsed with water. This material was recrystallized from a mixture of 350 ml. of 95% ethanol and 100 ml. of water. A total of 8.8 g. of o-benzylbenzoic acid (62.5% yield) was collected in five crops, the first melting 116-117°, the last, 114-116°. Literature m.p.: 113° (5).

**p-Tolyllithium in Ether.** Seventy-five milliliters of anhydrous ether was placed in a 200-ml. 3-necked flask fitted with a reflux condenser, a pressure equalizing dropping funnel, a nitrogen atmosphere, and a magnetic stirrer. The system was swept with nitrogen and 3.0 g. (0.433 g. atom) of lithium wire was cut into small pieces and allowed to fall directly into the ether in the flask. Nitrogen was swept through the system again, and a solution of 29 g. (0.171 mole) of p-bromotoluene in 30 ml. of anhydrous ether was added dropwise, with continuous stirring. The resulting dark suspension was allowed to settle for 30 minutes before use. A 0.8 ml. aliquot was titrated with 0.1079 N hydrochloric acid to a phenolphthalein end point and found to be 1.39 N.

**Reaction of 9,10'-Dichlorodianthracene with p-Tolyllithium.** A 25 ml. portion of 1.39 N p-tolyllithium in anhydrous ether was added to a solution of 3 g. (0.0071 mole) of 9,10'-dichlorodianthracene in warm anhydrous benzene under
a nitrogen atmosphere, and the resulting milky white mixture heated at reflux for 23 hours. At the end of this time, 100 ml. of distilled water was added cautiously and reflux continued for one hour. Upon cooling, the mixture was filtered to remove 0.68 g. (26.9%) of crude dianthracene, which after recrystal-
ization from benzene melted at 249-255° with sublimation and remelted at 210-
212°. The organic phase was separated, the solvent was evaporated, and the yellow oily residue taken up in 75 ml. of cyclohexene. The undissolved solid and the first crop of crystals from the cyclohexene solution melted above 330°,
 furnishing 0.625 g. of crude high melting hydrocarbon. A sample of this mater-
ial after sublimation at 225-240°, 0.04 mm. Hg, melted at 348°. The infrared
spectrum of the crude material indicated that it was the same as the hydro-
carbon isolated by E.C. Friedrich from this reaction (3).

When this reaction was repeated using 5 g. of 9,10'-dichlorodianthracene and the lower melting products exhaustively fractionally crystallized from cyclohexene, 1.57 g. of a crude thermally unstable white crystalline product was isolated. Its melting point behavior indicated that it was contaminated by a high-melting substance; neglecting this residue, the material melted at 215°, remelted at 160°. A portion of this material was recrystallized from a 1:1 mixture of benzene and cyclohexene. The first crop was discarded, for it was contaminated with the higher melting material. The second crop melted sharply at 220°, and remelted from 160-200°. The infrared spectrum of the melt of this material indicated that it was identical with a 1:1 molar mixture of 9-chloro-
anthracene with anthracene. The substance gave a strong positive Beilstein
test. It was therefore concluded to be 9-chlorodianthracene.

Reaction of 9,10'-Dichlorodianthracene with n-Butyllithium.- A 20 ml.
portion of 1.5 N n-butyllithium (manufactured by Foote Mineral Company, distilled and stored under an inert atmosphere in pentane-heptane solution) was added to a solution of 3.0 g. (0.0071 moles) of 9,10'-dichlorodianthracene in 300 ml. of warm anhydrous benzene under a nitrogen atmosphere. The mixture was heated at
reflux for 17 hours, after which time the excess lithium reagent was destroyed cautiously with distilled water and the mixture was allowed to stand for several hours. The solid at the interface was filtered off and found to be 0.225 g. (8.97% yield) of crude dianthracene (m.p. 275°, remelt 214-220°), a sample of which after one recrystallization from benzene melted at 290°, remelted at 212-215°. The amber organic layer was separated, dried briefly with Drierite, and evaporated partially on a steam bath. Upon cooling, crystals separated which were white after rinsing with acetone (m.p. 326-360°). This material was transferred to a test tube and pyrolyzed in an oil bath at above 300° until all material had either melted or sublimed. The pyrolyzate was recrystallized from benzene and yielded 0.033 g. of a hydrocarbon melting at 370°. The ultraviolet spectrum of this hydrocarbon was identical with that of 9,10′-dehydrodianthracene, having maxima at 290 and 268 mp and a pseudomax near 200 mp (1).

Anal.: Calcd. for C₃₀H₁₂₃: C, 94.88; H, 5.12.

Found: C, 95.07; H, 5.24

Nuclear Magnetic Resonance Spectra.—The two high-melting hydrocarbons from the reactions of phenyllithium and p-tolyllithium with 9,10′-dichlorodiantanthracene and the known hydrocarbon 9,10′-dehydrodianthracene were tested for solubility in a variety of organic solvents (CCl₄, CHCl₃, CH₂Cl₂, CS₂, liquid SO₂ and C₆H₆) both at room temperature and at elevated temperature, but only benzene dissolved any of the samples to a significant extent. A 3% solution of the phenyllithium hydrocarbon was obtained at steam bath temperature in a sealed tube. A trial run of this sample yielded no significant nuclear magnetic resonance signal, despite the fact that the sample did not crystallize for a considerable time after cooling. When attention was turned to the possibility of molten naphthalene as a solvent, it was discovered that an 8-10% solution of each of the above samples could be obtained at 110-150°. The solvent had the single disadvantage of subliming to the top of the sample tube to a
considerable extent when heated for long periods of time. Sample tubes were prepared asumming the three compounds to be the following: (Benzene rings are omitted for the sake of simplicity.)

As a qualitative and quantitative standard, ferrocene (Mol. Wt. 188, having 10 equivalent hydrogens) was used in molar concentration one-fifth that of the hydrocarbons, so that its peak area represented two hydrogens, provided the hydrocarbon molecular weights were correctly assigned.

Samples were weighed out as follows: Sample I contained 35.3 mg. of I, 3.75 mg. of ferrocene, and 39.4 mg. of naphthalene; Sample II contained 35.4 mg. of II, 3.75 mg. of ferrocene, and 37.4 mg. of naphthalene; Sample III contained 35.2 mg. of II, 3.7 mg. of ferrocene, and 390.4 mg. of naphthalene. The tubes were drawn out into fine capillaries and successively pumped down to 0.1 mm. Hg and flooded with high purity nitrogen three times each, after which the capillaries were sealed. This precaution was found necessary in order to prevent oxidation of ferrocene. A preliminary spectrum of II was run without ferrocene to ascertain the location of the peak from the hydrocarbon with respect to the solvent band, and to differentiate clearly the sample peak from that of the standard.
The spectra were obtained by heating the samples in a hot air stream directed along the sample tube from base to top as it spun on the dewar jacketed sample bearing within the Varian nuclear magnetic resonance recording spectrograph. Table I shows the raw data obtained from measurement of the spectra of the samples prepared. Spectra were run in duplicate at different gains, designated A and B. Areas were measured by cutting out and weighing five tracings of each peak.

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<tbody>
<tr>
<td>I</td>
<td>146°</td>
<td>A</td>
<td>4.97</td>
<td>2.02</td>
<td>1.89</td>
<td>2.00</td>
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<tr>
<td></td>
<td></td>
<td>B</td>
<td>5.02</td>
<td>1.89</td>
<td>2.02</td>
<td>2.00</td>
</tr>
<tr>
<td>II</td>
<td>113°</td>
<td>A</td>
<td>4.99</td>
<td>0.73</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td></td>
<td></td>
<td>B</td>
<td>5.02</td>
<td>0.92</td>
<td>2.00</td>
<td>2.00</td>
</tr>
<tr>
<td>III</td>
<td>118°</td>
<td>A</td>
<td>4.99</td>
<td>0.35</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td></td>
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<td>B</td>
<td>5.02</td>
<td>0.487</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td></td>
<td></td>
<td>A</td>
<td>7.59</td>
<td>1.21</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td></td>
<td></td>
<td>B</td>
<td>7.64</td>
<td>1.47</td>
<td>2.00</td>
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The above data were interpreted to indicate that the structures of II and III were one of the following possibilities:

\[ \text{II: } \text{Ar} = \text{Phenyl} \]
\[ \text{III: } \text{Ar} = \text{p-Tolyl} \]

Thus the postulated molecular weights were in error. When the areas were corrected for the error in assumed molarity ratios, the data in Table II were obtained.
Table II

<table>
<thead>
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<tbody>
<tr>
<td>II</td>
<td>115°</td>
<td>4.99</td>
<td>0.88</td>
<td>1.12</td>
<td>2.00</td>
<td>2.00</td>
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<tr>
<td>(Average)</td>
<td>5.00</td>
<td>1.00</td>
<td></td>
<td></td>
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</tbody>
</table>

| III    |       |        |       |            |      |           |
|        |       |        |       |            |      |           |
| A      | 4.99  | 0.442  | 2.00  |            |      |           |
|        | B     | 4.99   | 0.615 | 2.00       |      |           |
| (Average) | 4.99 | 0.528  |       |            |      |           |

|       |       |        |       |            |      |           |
| A      | 7.59  | 1.53   | 2.00  |            |      |           |
| B      | 7.64  | 1.86   | 2.00  |            |      |           |
| (Average) | 7.62 | 1.695  |       |            |      |           |

When the aryl -CH$_3$ peak is taken as an internal standard of area 3.00 in Sample III, the bridgehead hydrogen peak has a relative area of 0.936.
IV. Bibliography


4. R. Little, unpublished research.


Summary

Evidence has been found which is consistent with the hypothesis that the reduction of 9,10'-dibromodianthracene to dianthracene by lithium aluminum hydride proceeds by a carbonium ion mechanism. It was found that working up the reaction mixture with deuterium oxide resulted in no significant amount of deuterium incorporation in the product, but that using lithium aluminum deuteride as the reducing reagent resulted in nearly quantitative deuterium incorporation. The possibility that the reaction may proceed by an elimination to form a bridgehead olefin, to which lithium aluminum deuteride then adds, has not been ruled out. However the fact that the infrared spectrum of the product is identical to that of dianthracene-9,10'-D₂, and that the infrared spectrum of the monomer resulting from decomposition of the product is identical to that of anthracene-9-D strongly suggests that the product is not a mixture of dianthracene-9,10-D₂ and dianthracene-9,10'-D₂, which one would expect to obtain from the elimination addition mechanism. The other, more probable, mechanism, generation of a carbonium ion on the bridgehead carbon atom which then attacks lithium aluminum deuteride, appears to be analogous to a reaction of silver nitrate with 9,10'-dibromodianthracene in the same solvent (tetrahydrofuran) in the presence of ethanol. In that reaction, silver bromide is produced, and an organic product is formed which appears from its infrared spectrum to be an aliphatic ether.

Evidence has been obtained which rules out the possibility of a bridgehead olefin intermediate in the formation of 9-n-butyldianthracene from 9,10'-dibromodianthracene by treatment with n-butyllithium. It was found that when 9,10'-dibromodianthracene-9',10-D₂ was used as starting material, the compound 9-n-butyldianthracene-9',10-D₂ was obtained.
The products of the reaction of 9,10'-dichlorodianthracene with 
n-butyllithium have been found to be n-butylidianthracene (7%) and 
dianthracene (84.8%).

The course of the reaction of 9,10'-dichlorodianthracene with 
phenyllithium has been found to be altered in favor of the highmelting 
hydrocarbon known to be a product of that reaction by removing the ether 
added with the phenyllithium at the outset of the reaction. This suggests 
that competing reagents proceed more readily in a polar medium, and that 
they may indeed be reactions with ether itself.

Two routes to preparation of an analog of the above mentioned hydro-
carbon in which the aromatic ring is activated have been attempted. The 
value of such an analog would be that it might be oxidized under con-
ditions which would leave the dimeric structure intact but would remove 
the substituent aryl group. It was hoped that decarboxylation of the 
product of such an oxidation would lead to 9,10' (or 10)-dehyrodianthracene, 
and that the structure of the hydrocarbons would be resolved. In the 
first attempt, lithium p-lithium phenoxide was used, but failed to attack 
9,10'-dichlorodianthracene under the conditions used for the phenyllithium 
reaction. In the second attempt, 2,6-dimethoxyphenyllithium was used and 
although it did not attack the dimer under the usual conditions, reaction 
did occur when a higher boiling solvent was used. However, no analog to 
the highmelting hydrocarbon of the phenyllithium reaction was isolated. 
Since ether was distilled from this reaction mixture at the outset (a 
condition which was found to improve the yield of the phenyllithium 
hydrocarbon), the failure of this route can probably be attributed to
the steric hindrance of the two methoxyl groups ortho to the lithium function.

A number of attempts have been made to prepare 9-fluoroanthracene by nucleophilic substitution off the 9- position of anthracene. Anhydrous potassium fluoride was used as the source of fluoride ion. However, under very vigorous conditions no reaction was found to occur with 9-bromoanthracene, and none of the desired reaction was found with 9-nitroanthracene. Although the route of substitution on 9,10'-dibromodianthracene looks promising in light of the findings mentioned earlier that indicate the possibility of carbonium ion generation, no reaction was found when the dimer was exposed to anhydrous potassium fluoride in anhydrous tetrahydrofuran for three days at reflux temperature.
Appendix - Experimental

Reaction of 9,10'-Dibromodianthracene with Lithium Aluminum Hydride

Hydride followed by Deuterium Oxide.- According to the method of D.E. Applequist (1), 1.000 g. (0.00195 mole) of 9,10'-dibromodianthracene was dissolved in 90 ml. of anhydrous tetrahydrofuran in a flask fitted with a reflux condenser, pressure equalizing dropping funnel, magnetic stirrer and constant pressure nitrogen atmosphere. Approximately 0.8 g. (0.021 mole) of lithium aluminum hydride was added to the solution, which was then stirred and heated at reflux for six hours. Through the dropping funnel 4 ml. (0.2 mole) of deuterium oxide was then added cautiously to the reaction mixture. Stirring was continued overnight, after which time dilute sulfuric acid was added to dissolve the salts present. The resulting three phase mixture was diluted with 100 ml. of benzene and filtered to remove 2.38 g. of white solid. Upon recrystallization of this material from benzene, a total of 226.5 mg. of white solid, melting 268-270°, was isolated in two crops. This product was heated in a sublimator until all material had melted or sublimed, and the residue was sublimed at 20 mm. Hg, 110-130°. The anthracene thus obtained was submitted for deuterium analysis by the falling drop method.

Anal.: Calcd. for C_{14}H_{9}D: D, 10.00 atom %. Found: D, 0.4%.

When this experiment was repeated on a smaller scale using a modification of the above procedure such that no acid or water but only deuterium oxide came in contact with the reaction product, again only a trace of deuterium was found in the anthracene resulting from monomerization of the dianthracene produced.
Reaction of 9,10'-Dibromodianthracene with Lithium Aluminum Deuteride.

To a solution of 0.5745 g. (0.00112 mole) of 9,10'-dibromodianthracene in 100 ml. of anhydrous tetrahydrofuran in a flask fitted with a reflux condenser, pressure equalizing dropping funnel, magnetic stirrer and constant pressure nitrogen atmosphere, was added 0.30 g. (0.00715 mole) of 95.0% lithium aluminum deuteride. The reaction mixture was stirred and heated at reflux for two hours. Heating was then stopped, and stirring was continued overnight. To the lemon yellow suspension 10 ml. of deionized water was added cautiously from the dropping funnel. The resulting yellow slurry was filtered by suction, air dried, and transferred to a soxhlet thimble from which it was extracted with benzene for 24 hours. The benzene deposited 170.9 mg. of dianthracene-9,10'-D₂, which was identified by comparison of its infrared spectrum with that of the known compound. This sample was dried and submitted for deuterium analysis by the falling drop method. Further extraction of the residue in the soxhlet thimble for three days afforded another 84.3 mg. of crystals whose infrared spectrum was identical to that of the first crop. The melting point of this material was 176-179°, with a small residue melting at 322°. The total yield of dianthracene-9,10'-D₂ isolated was thus 64%.

**Anal.:** Calcd. for C₂₈H₁₅D₂: D, 10.00 atom %. Found: D, 9.00 atom %.

Since the deuterium analysis was low, it seemed possible that the sample might be contaminated with 9,10'-dehydrodianthracene (although no indication of the presence of that substance was seen in the infrared spectrum). The sample was therefore pyrolyzed in a small sublimator, and the monomer was allowed to sublime at atmospheric pressure. The anthracene-9-D thus obtained was submitted both for deuterium analysis and for an infrared spectrum. A sample of known anthracene-9-D prepared by R. Little (2) was submitted for an infrared spectrum for comparison. The spectra obtained were identical.
Anal.: Calcd. for \( \text{C}_{14}\text{H}_9\text{D}_1 \): D, 9.50 to 10.00 atom %. Found: D, 9.26 atom %.

Reaction of 9,10'-Dibromodianthracene with Silver Nitrate.—A solution of 0.3 g. (0.0006 mole) of 9,10'-dibromodianthracene in 50 ml. of warm anhydrous tetrahydrofuran was diluted with 25 ml. of absolute ethanol, and to it was added 0.2 g. (0.0012 mole) of silver nitrate. This mixture was shielded from light and heated at reflux for 15\( \frac{1}{2} \) hours. The mixture, now cloudy and light brown, was diluted with 50 ml. of deionized water and 150 ml. of ether was added. The mixture was transferred to a separatory funnel and the clear aqueous phase was drained off. The organic phase and interfacial solid was decanted onto a filter. The dried solid was rinsed with dilute ammonium hydroxide and filtered. The filtrate clouded upon acidification with dilute nitric acid. The ether solution was evaporated to a volume of 30 ml. and filtered to remove 0.28 g. of white solid, m.p. 222°.

The nujol infrared spectrum of this substance indicated that it contained starting material, but strong broad bands of a new substance were present.

The KBr disc infrared spectrum had bands at 1458 and 1472 cm\(^{-1}\) (in the region of \( \text{CH}_3 \)- and \( \text{CH}_2 \)- deformation) and a sharp band at 1264 cm\(^{-1}\) (in the region of aliphatic ether C-O stretching). This compound's infrared spectrum was very similar to spectra of compounds isolated in small yields from the reaction mixtures resulting from treatment of 9,10'-dichlorodianthracene with phenyl-, p-tolyl- and n-butyllithium.

Reaction of 9,10'-Dibromodianthracene-9',10-D\(_2\) with n-Butyllithium.—The starting material 9,10'-dibromodianthracene-9',10-D\(_2\), prepared by R. Little (2), was found to contain 94.6\% of the calculated amount of deuterium.

A solution of 0.931 g. (0.00184 mole) of this compound in 100 ml. of warm anhydrous benzene was prepared, and to it 15 ml. of a 0.75 M solution of n-butyllithium
in pentane, prepared according to the method of D.E. Applequist (1), was added by pipette. The cloudy yellow mixture was allowed to stand overnight without heating (10½ hours). To the pale yellow mixture, now containing considerable white precipitate, was added 100 ml. of deionized water. The organic layer was separated and filtered to remove 87.1 mg. of gray solid whose melting point, 278°, and infrared spectrum showed it to be dianthracene-9,10'-D₂. A second crop of the same compound weighing 76.2 mg. separated upon concentration of the organic layer to half its original volume. The filtrate of this material was evaporated to dryness in an air stream and the resulting sticky yellow solid (0.72 g.) was rinsed onto a filter with a little pentane. The undissolved solid (0.22 g.) was nearly white and no longer sticky. It was extracted with 50 ml. of a solvent containing 2/3 acetone and 1/3 methanol by volume, and filtered. The filtrate was boiled down to a volume of 7 ml. and cooled. There separated 100.0 mg. of very pale yellow solid, melting 184-187°, whose infrared spectrum indicated it to be a mixture of dianthracene-9,10'-D₂ and 9-n-butyldianthracene-9',10'-D₂. From the filtrate of this material was obtained a second crop of nearly white solid, m.p. 176-180°. The infrared spectrum of this material was free from dianthracene-9,10'-D₂ bands, and was very similar to that of known 9-n-butyldianthracene except for a sharp band at 721 cm⁻¹. This compound was submitted for analysis after thorough drying in an Abderhalden apparatus.

**Anal.:** Caclcd. for C₂₂H₂₆D₂: C, 92.71%; H, 6.75%; D, 7.14 atom %.

**Found:** C, 91.82%; H, 6.82%; D, 6.47 atom %.

Although only 90.6% of the theoretical deuterium content was found, it should be recalled that the starting material contained only 94.6% of the theoretical amount. The product is therefore only 4.0 relative % deficient.

The residue from the acetone-methanol extraction was 20.3 mg. more of dianthracene-9,10'-D₂. The total yield of this substance isolated pure was 29.4%.
Reaction of 9,10'-Dichlorodianthracene with n-Butyllithium.- To a solution of 1.00 g. (0.0024 mole) of 9,10'-dichlorodianthracene in 100 ml. of warm anhydrous benzene was added 15 ml. of a 0.702 M solution of n-butyl lithium in pentane prepared by the method of D.E. Applequist (1). The mixture was heated at reflux under a nitrogen atmosphere for 15 hours. Excess lithium reagent was destroyed by addition of 100 ml. of deionized water and the mixture was allowed to cool. The organic layer with suspended solid was separated and washed twice with 100 ml. portions of deionized water. The organic mixture was then filtered to remove 669.5 mg. of white solid, m.p. 275-280°, whose infrared spectrum confirmed its identity as dianthracene. Evaporation in vacuo of the clear benzene filtrate left 0.42 g. of a yellow oil in which some solid was suspended. The oil was diluted with 50 ml. of absolute methanol and 20 ml. of reagent grade acetone, heated on a steam bath, and filtered to remove 38.9 mg. of white solid whose infrared spectrum and melting point (268-270°) identified it as dianthracene. Thus dianthracene was obtained in 84.8% yield. All attempts to crystallize the methanol-acetone soluble oil failed. In another experiment, however, from the oily residue isolated as above in a reaction run on the same scale in a similar fashion, 70.8 mg. of white solid was obtained whose infrared spectrum indicated it to be crude 9-n-butyldianthracene in approximately 7% yield.

Reaction of Phenyllithium with 9,10'-Dichlorodianthracene.- To a solution of 1.3835 g. (0.00326 mole) of 9,10'-dichlorodianthracene in 150 ml. of anhydrous benzene was added by pipette 30 ml. of a freshly prepared 1.18 M phenyllithium in ether prepared by the method of Organic Reactions(3). The milky white reaction mixture was then heated, and from it solvent was distilled until the vapor temperature was 75°. At least 55 ml. of solvent had been removed at that point. The reaction flask was then closed under
nitrogen and heated at reflux for 12½ hours, after which time the dark brown mixture was washed with 100 ml. of deionized water. The clear aqueous phase was separated and the yellow organic phase was filtered to remove 0.2081 g. of dianthracene (m.p. 283-287°). A second crop of 52.7 mg. of dianthracene (m.p. 270-273°) was obtained by concentrating the organic filtrate to 50 ml. A third crop of solid (m.p. 280-282°) isolated by further concentration of the organic filtrate appeared from its infrared spectrum to be crude dianthracene contaminated by the unknown highmelting hydrocarbon which is known to be a product of this reaction. The total yield of crude dianthracene isolated was thus 26.7%. Further crops of solids were obtained by fractional crystallization of the reaction products from more polar solvents. A total of 0.5628 g. of solid, isolated in seven crops and melting as high as 316-320° and as low as 240°, was obtained, all of which had infrared spectra essentially identical to that of the unknown highmelting hydrocarbon known to be a product of this reaction. Assuming the structure of this hydrocarbon to be 9-phenyl-9′,10 (or 10′)-dehydrodianthracene, this product was obtained in crude form in 38.8% yield, approximately twice the yield obtained in previous reactions in which ether was not distilled from the reaction mixture at the outset of the reaction. No further solid products were isolated from this reaction mixture, for although there was clearly more material present, it oiled repeatedly.

9-Chloroanthracene,- According to the method of B.M. Mikhailov and M.S. Promyslov (4), a mixture of 100 g. (0.561 mole) of once recrystallized technical grade anthracene, 140 g. (0.672 mole) of phosphorus pentachloride, and 2500 ml. of anhydrous benzene was prepared in a 5 l. flask fitted with a reflux condenser and a drying tube. The flask was
immersed in a hot water bath in a well-ventilated hood, and heated for 1 hour. The resulting red solution was cooled in a water bath for 1 hour, after which time a yellowish crystalline substance was filtered off and found to be 34 g. of anthracene, m.p. 210-217°. The filtrate was washed with 5 l. of water, and the now cloudy yellow organic layer was separated and placed in a solvent stripper to remove the benzene. The yellow residue was extracted with 3 l. of boiling methanol, and the yellow solution was filtered and allowed to cool. From it in successive crops 41 g. of 9-chloroanthracene was obtained, the first crop melting at 106°, the last, 95-100°. The reported m.p. is 106°(4). A 34.4% yield was obtained, half that reported in the literature.

9,10'-Dichlorodianthracene - A solution of 40 g. (0.189 mole) of 9-chloroanthracene in 450 ml. of anhydrous benzene was divided, placed in two tightly stoppered pyrex flasks, and set in a sunny place. After 17 days, 24.78 g. of yellowish crystals were collected which, after recrystallization from benzene, melted 228-230° and remelted 107-108°. Although the filtrate was cleaned with darco and returned to the sun, no further product was obtained after several weeks' exposure to sunlight. A 62% yield of the dimer was obtained.

Lithium p-Bromophenoxide - To a solution of 17.3 g. (0.10 mole) of p-bromophenol in 200 ml. of anhydrous ether in a 500 ml. three neck flask equipped with reflux condenser and nitrogen atmosphere was added 200 ml. (0.117 mole) of 0.583 M n-butyllithium in ether, prepared according to the method of Organic Reactions (5). A gas (presumably butane) escaped through the condenser, and the white salt precipitated. This salt did not
dissolve in 500 ml. of anhydrous ether at reflux temperature. Therefore 250 ml. of anhydrous tetrahydrofuran was added and the ether was distilled out. The salt still did not dissolve, so another 250 ml. of tetrahydrofuran was added. Although no clear solution was obtained, the salt formed a very fine suspension which settled only after many hours, and then not completely.

**Lithium p-lithium phenoxide.**—The two day old suspension of lithium p-bromophenoxide (0.10 mole) in tetrahydrofuran was transferred by pipette to a 500 ml. pressure equalizing dropping funnel which had been dried carefully. The funnel was fitted to a dry 3 l. three neck flask fitted with a reflux condenser, into which was pipetted 150 ml. (0.138 mole) of freshly prepared 0.92 M n-butyllithium in ether, prepared by the method of Organic Reactions (5). The flask was heated to reflux temperature and the salt slurry in the funnel was added in a slow stream over a period of thirty minutes. The mixture was stirred with a magnetic stirrer and heated at reflux for one hour longer. The yellowish suspension was titrated with hydrochloric acid to a phenolphthalein end point and was found to be 0.40 N or 0.20 M, slightly higher than the expected 0.18 M, probably due to some solvent escape.

**Reaction of Lithium p-Lithium Phenoxide with 9,10'-Dichlorodithracene.**—A solution of 10.00 g. (0.0237 mole) of 9,10'-dichlorodithracene in 1 l. of anhydrous benzene was prepared and added to a solution of approximately 0.1 mole of lithium p-lithium phenoxide in tetrahydrofuran and ether. The yellow solution was heated at reflux for 20 hours, after which time the mixture, now cloudy and rose colored, was treated with 1 l. of deionized water. The aqueous phase was an intense dark red; the organic
phase was cloudy and white. After standing overnight, the three phase system was filtered to remove 85.5 mg. of beautiful flat white prisms, melting at 228° and remelting at 110°. Removal of solvent from the organic phase resulted in recovery of 82.5% of the dimeric starting material. Acidification of the aqueous layer and extraction with ether produced, upon removal of the solvent, a dark brown oil which was halogen free. (Bellstein test) and which formed a solid derivative with bromine water which, in crude form, melted 81-87°. The reported melting point of tri-bromophenol is 95° (6). The possibility that the oil was p-n-butylphenol is unlikely, for it distilled over a range up to 240° and the reported boiling point of p-n-butylphenol is 248°(7). Thus, although the desired lithium reagent seems to have been present, it failed to attack the dimer under the reaction conditions used.

2,6-Dimethoxyphenyllithium in ether.- Phenyllithium in ether was prepared according to the method of Organic Reactions (3) and was found to be 1.37 M by titration to a phenolphthalein end point. A 2 l. three neck flask was fitted with reflux condenser and constant pressure nitrogen atmosphere. A 150 ml. portion of the freshly prepared solution of phenyllithium was transferred to the flask, and to it was added 27.6 g. (0.20 mole) of resorcinol dimethyl ether. The solution was allowed to stand for 60 hours (according to the method of Organic Reactions) (8), during which time the originally dark solution grew lighter and a precipitate formed on the walls of the flask. The unused phenyllithium solution standing in an adjacent flask under nitrogen retained its dark red color and formed no precipitate over this time.
Reaction of 9,10'-dichlorodianthracene with 2,6-Dimethoxyphenyllithium.

A solution of 10.0 g. (0.0237 mole) of 9,10'-dichlorodianthracene in 400 ml. of hot m-xylene was prepared and boiled to remove any water present. The solution was added to approximately 0.2 mole of 2,6-dimethoxyphenyllithium in ether, and from the resulting milky suspension ether was distilled until the temperature of the liquid was 120°. The reaction vessel was then closed under nitrogen and the mixture was heated at reflux for 23 hours. The mixture, tan with considerable white solid suspended, was then cooled and washed with 500 ml. of deionized water. Both phases had strong purple iridescence. The mixture was filtered to remove 3.91 g. of a tan solid (m.p. 272-275°, remelting 212-224°) whose infrared spectrum showed it to be dianthracene in 46.7% yield. The organic layer was separated, washed with an equal volume of deionized water, and placed in a solvent stripper under 5 mm. Hg pressure at steam bath temperature. After removal of all solvent, the residue, a brown oil which solidified to a gummy mass, weighed 15.20 g. Upon extraction with 3 l. of methanol and removal of the solvent, 5.22 g. of oily solid was isolated which, upon recrystallization from absolute ethanol, sintered at 87°, melting by 100° to a black tar. Oxidation of a little of this material with sodium permanganate in reagent grade acetone produced no solid acid, and only a small amount of starting material (3%) was recovered. The residue from the methanol extract was taken up in cyclohexene, but successive concentrations and cooling produced only one crop of crystals, 12 mg. of crude dianthracene. The solvent was therefore removed and 5.67 g. of a tan glass was obtained. When 1.62 g. of this glass was dissolved in reagent grade acetone and oxidized with 10 g. of sodium permanganate, only 0.24 g. of tan solid was obtained, melting.
90-100° to a black tar. The infrared spectrum of this compound did not indicate the presence of a carboxyl group.

Reaction of 9-Bromoanthracene with Potassium Fluoride in Diglyme.- Approximately 100 ml. of diglyme was distilled from lithium aluminum hydride into the reaction flask, which had been oven dried, and to it was added 1.0225 g. (0.00257 mole) of 9-bromoanthracene and 10.0 g. (0.172 mole) of anhydrous potassium fluoride. This mixture was heated at reflux under nitrogen for 36 hours and allowed to cool. A ten milliliter portion was removed by pipette and diluted with an equal volume of distilled water, precipitating yellow solid. The mixture was extracted with two 10 ml. portions of ether; the yellow extract was dried and evaporated to leave a yellow solid (m.p. 93-95°) whose melting point was not depressed by starting material. The infrared spectrum of the product indicated it to be pure 9-bromoanthracene. The aqueous phase from the extraction failed to give a precipitate with silver nitrate. Thus no reaction had occurred.

The remainder of the reaction mixture was transferred to a bomb tube, sealed under nitrogen, and heated in an oven at 250° for 8 hours. After cooling overnight, the tube was opened and the contents worked up as above. The yellow solid isolated (m.p. 98°) showed no melting point depression when mixed with starting material. Again, the aqueous phase failed to give a precipitate when treated with silver nitrate. When this reaction was repeated in a sealed tube at 325° for 24 hours, as before, only starting material was recovered.

Reaction of 9-Nitroanthracene with Potassium Fluoride in Acetonitrile.- A mixture of 5.0 g. (0.086 mole) of anhydrous potassium fluoride, 300 ml. of acetonitrile and 5.0 g. (0.0224 mole) of 9-nitroanthracene was heated
at reflux for 20 hours. The reflux temperature was observed to be unchangeing during this period. Removal of part of the solvent, dilution with water and extraction with ether gave a yellow extract which, upon evaporation, deposited 4.93 g. of starting material which was recrystallized from ethanol and collected in three crops, the first melting 157°, the last, 151-153°. The infrared spectrum of this product showed it to be 9-nitroanthracene.

Reaction of 9-Nitroanthracene with Potassium Fluoride in Diglyme.- A mixture of 5.0 g. (0.086 mole) of anhydrous potassium fluoride, 5.0 g. (0.00224 mole) of 9-nitroanthracene and 25 ml. of freshly distilled diglyme was sealed in a bomb tube under nitrogen and heated at 300° for 15 hours. After cooling, the bomb tube was opened and the black tarry contents were washed into a separatory funnel with 200 ml. of ether and 200 ml. of water. The organic layer, dark brown, was cleaned with norite, filtered, filtered again over alumina, and found to be unimproved in color. The ether was evaporated on a steam bath and the residual brown oil was extracted with 200 ml. of hexane. The extract was dark red. The brown solid filtered off melted at 195°, but its infrared spectrum was not that of anthracene or anthraquinone or 9-nitroanthracene. Since its melting point is far above that reported for 9-fluoroanthracene, further investigation of this product was not pursued.

Reaction of 9,10'-Dibromodianthracene with Potassium Fluoride.- A mixture of 1.00 g. (0.00194 mole) of 9,10'-dibromodianthracene, 2.0 g. (0.0344 mole) of anhydrous potassium fluoride and 100 ml of freshly distilled anhydrous tetrahydrofuran was heated at reflux under nitrogen for three days. A 1 ml. aliquot of the cooled supernate was removed by
pipette, diluted with 5 ml. of deionized water, filtered, and the cloudy filtrate cleared by addition of acetone. Addition of alcoholic silver nitrate solution caused no precipitate. The solvent was therefore distilled from the reaction flask and replaced by 100 ml. of freshly distilled diglyme. The resulting mixture was heated at reflux under nitrogen for 15½ hours. When tested as above for the presence of bromide ion, the supernate gave negative results once more.

**Nuclear Magnetic Resonance Spectra.**—Since the sample designated earlier in this thesis as III, the highmelting hydrocarbon obtained from the p-tolyl lithium reaction, appeared from the data in Table I not to have been entirely dissolved at the time its nuclear magnetic resonance spectrum was observed, the same sample was resubmitted and relative areas measured on the new spectrum in a manner similar to that described for the earlier spectra. The results are tabulated below.

<table>
<thead>
<tr>
<th>Peak Assignment</th>
<th>Bridgehead $-\text{H}$</th>
<th>Aryl $-\text{CH}_3$</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Area</td>
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<td>2.372</td>
<td>2.00</td>
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<tr>
<td>Relative Conc.</td>
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<td>0.793</td>
<td>2.00</td>
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<tr>
<td>Relative Area</td>
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<td>2.00</td>
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<tr>
<td>per Mole</td>
<td></td>
<td></td>
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Bibliography


2. R. Litle, unpublished research.


